PATENT ABSTRACTS OF JAPAN

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(54) SEMICONDUCTOR CLEANING AGENT

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a semiconductor cleaning agent for removing a residual generating in etching, etc., in a process for manufacturing an element using a ferroelectric material.
SOLUTION: This semiconductor cleaning agent is composed of a water solution containing policarboxylic acid which is used for removing the residual which generates in the process for manufacturing the element using the ferroelectric material.

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CLAIMS

[Claim(s)]
[Claim 1] The cleaning agent for semi-conductors which is used in case the residue object generated in the production process of the component using a ferroelectric ingredient is removed and which consists of a water solution containing polycarboxylic acid.
[Claim 2] The cleaning agent for semi-conductors according to claim 1 whose polycarboxylic acid is oxalic acid.
[Claim 3] Furthermore, the cleaning agent for semi-conductors containing a fluorine compound according to claim 1.
[Claim 4] The cleaning agent for semi-conductors according to claim 1 whose ferroelectric ingredient is a tantalic acid strontium bismuth.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention is the nonvolatile memory production process which used the ferroelectric, and relates to the cleaning agent for semi-conductors used for removal of the residue object generated at the time of etching etc.
[0002]
[Description of the Prior Art] Since the data remembered that the memory currently used abundantly at the computer etc. turns off the power conventionally were eliminated, it always energized or the power source for backup was needed. However, the nonvolatile memory which used the ferroelectric ingredient was developed in recent years. This nonvolatile memory is considered in the use to file memory, personal IC card, and mobile communication equipment, a Personal Digital Assistant device, AV personal computer, etc. As a ferroelectric ingredient which is the important point of nonvolatile memory, PZT (called PZT for short), a tantalic acid strontium bismuth (called SBT for short), etc. are used. Moreover, properties, like adhesion with the substrate and ferroelectric of ** silicon dioxide with high ** diffusion barrier property with low ** reactivity with high ** thermal resistance with the mismatch of a lattice constant with ** ferroelectric ingredient with sufficiently small ** electric resistance small as an electrode material of the nonvolatile memory which used the ferroelectric etc. is good are required, and platinum (Pt), ruthenium oxide (RuOx), oxidization iridium (IrO2), etc. are used.
[0003] For this reason, the residue object generated in a nonvolatile memory production process at the time of etching etc. becomes a thing containing these metals, removal of a residue object is very difficult, and the technique of removing these residue objects is needed. In order to remove these residue objects, generally the approach of removing with the amine system exfoliation liquid which usually contains a hydroxylamine is enforced. However, the amine system exfoliation liquid containing a hydroxylamine has many troubles in respect of safety and an environment, and it also has the trouble of having to use it under still elevated temperature conditions.
[0004]
[Problem(s) to be Solved by the Invention] The technical problem of this invention is offering the cleaning agent for [which is used for the approach of removing the residue object generated in a nonvolatile memory production process at the time of etching etc. / which was safe and was excellent also in the environmental side] semi-conductors.
[0005]
[Means for Solving the Problem] this invention persons found out that the water solution containing polycarboxylic acid might suit the purpose as a cleaning agent for semi-conductors, as a result of repeating examination wholeheartedly, in order to solve the above-mentioned purpose. This invention is completed based on this knowledge. That is, this invention offers the cleaning agent for semi-conductors which is used in case the residue object generated in the production process of a component which used the ferroelectric ingredient is removed and which consists of a water solution containing polycarboxylic acid.
[0006]
[Embodiment of the Invention] The polycarboxylic acid used in the cleaning agent for semi-conductors of this invention may be used independently, or may combine two or more sorts. As such

polycarboxylic acid, partial saturation dicarboxylic acid, such as saturation dicarboxylic acid, such as oxalic acid, a malonic acid, a succinic acid, a glutaric acid, an adipic acid, a pimelic acid, a SUPERIN acid, an azelaic acid, a sebacic acid, Ung decanedioic acid, and a DODEKANNI acid, a maleic acid, a fumaric acid, an itaconic acid, a citraconic acid, mesaconic acid, and glutaconic acid, is mentioned. In the above-mentioned polycarboxylic acid, it is oxalic acid especially preferably. Although especially a limit does not have the content of the polycarboxylic acid used for this invention and it is suitably chosen according to a situation, it is usually 0.1 - 15 % of the weight, and is 1 - 5 % of the weight preferably. If this amount has the slow removal rate of a residue object at less than 0.1 % of the weight and exceeds 15 % of the weight, since the problem of polycarboxylic acid depositing occurs, it is not desirable.

[0007] While the above-mentioned substrate is immersed into the approach immersed, for example into a cleaning agent as the removal approach of the residue object by this cleaning agent in the substrate using the ferroelectric ingredient which the residue object generated, and a cleaning agent, the approach of agitating a cleaning agent etc. can be mentioned with supersonic vibration, an impeller, etc. Moreover, although it is good at the temperature of the arbitration from a room temperature to the boiling point, 90 degrees C is desirable from ordinary temperature, and 20-70 degrees C is [that what is necessary is just to select the temperature of a cleaning agent suitably, judging from the condition of an extant residue object] usually especially desirable. Furthermore, there is no removal processing time and it should just choose especially a limit suitably according to the removal approach, the temperature of a cleaning agent, etc.

[0008] After removing a residue object using this penetrant remover, as a rinse to be used, it is enough with water, and there is no need of using an organic solvent like alcohol. Moreover, according to the presentation of a residue object, and a property, a surfactant, a chelating agent, a fluorine compound, etc. may be suitably added to this cleaning agent.

[0009] Furthermore, a fluorine compound can be made to contain by request in order to raise the removal ability of the residue object of the cleaning agent of this invention. As this fluorine compound, fluoric acid, ammonium fluoride, a hydrofluoric acid, ammonium hydrogendifluoride, ammonium fluoroborate, etc. are mentioned.

[0010] This fluorine compound may be used independently and may be used combining two or more sorts. Moreover, although what is necessary is for the content not to have especially a limit and just to choose suitably according to a situation, it is usually 0.001 - 10 % of the weight, and is 0.01 - 1 % of the weight preferably. At less than 0.001 % of the weight, when there is a possibility that improvement in the removal ability of a residue object may not fully be demonstrated and it exceeds 10 % of the weight, there is a possibility of causing the corrosion of an electrode, Si substrate, etc.

[0011]

[Example] Next, although an example explains this invention to a detail, this invention is not limited at all by these examples. In addition, drawing 1 shows a part of production process of the memory which used the ferroelectric ingredient. Drawing 2 is a typical sectional view of a component where the residue object after forming metal wiring used in the example and the example of a comparison exists. A part of production process of the memory shown in drawing 1 forms an insulating layer 5 on the Si substrate 6, and it forms the lower electrode 4 on it. Furthermore, after forming the ferroelectric ingredient 3 on it and forming the up electrode 2 subsequently, it covers by the insulating layer 1. Then, although the various metal wiring 8 is formed by dry etching, O2 ashing, etc., as shown in drawing 2 , the residue object 7 containing a metal, the organic substance, etc. generates, and it adheres on a substrate at that occasion.

[0012] Although 40 degrees C was immersed for 5 minutes in the component shown in example 1 drawing 2 into the water solution containing 3.4 % of the weight of oxalic acid, ultrapure water performed the rinse after that and SEM observation after desiccation was performed, it was checked that the residue object is removed completely.

[0013] Although 50 degrees C was immersed for 1 minute in the component shown in example 2 drawing 2 into the penetrant remover which is a water solution containing 3.4 % of the weight of oxalic acid, ultrapure water performed the rinse after that and SEM observation after desiccation was performed, it was checked that the residue object is removed completely.

[0014] 40 degrees C and 5-minute immersion were performed into the penetrant remover which is a

water solution which contains 5.5 % of the weight of oxalic acid for the component shown in example 3 drawing 2 . Although ultrapure water performed the rinse after that and SEM observation after desiccation was performed, it was checked that the residue object is removed completely.
[0015] Although 40 degrees C was immersed for 1 minute in the component shown in example 4 drawing 2 into the penetrant remover which is a water solution containing 3.4 % of the weight of oxalic acid, and 0.2 % of the weight of ammonium fluorides, ultrapure water performed the rinse after that and SEM observation after desiccation was performed, it was checked that the residue object is removed completely.
[0016] 50 degrees C and 10-minute immersion were performed into the penetrant remover which contains 3.4 % of the weight of citric acids for the component shown in example of comparison 1 drawing 2 . Then, although ultrapure water performed the rinse and SEM observation was performed after desiccation, most reduction of a residue object was not observed.
[0017] 50 degrees C and 10-minute immersion were performed into the penetrant remover which contains 3.4 % of the weight of tartaric acids for the component shown in example of comparison 2 drawing 2 . Then, although ultrapure water performed the rinse and SEM observation was performed after desiccation, most reduction of a residue object was not observed.
[0018]
[Effect of the Invention] The cleaning agent for semi-conductors of this invention can be removed easily, without corroding the residue object generated in the production process of a component which used the ferroelectric ingredient for a wiring material etc.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the typical sectional view of a component showing a part of production process of the memory which used the ferroelectric ingredient.
[Drawing 2] It is the typical cross section of the component in the condition that the residue object after forming metal wiring exists.
[Description of Notations]
One insulating layer, 2 up electrodes, about 3 dielectric materials, 4 lower electrodes, five insulating layers, 6Si substrate, 7 residue object, 8 metal wiring

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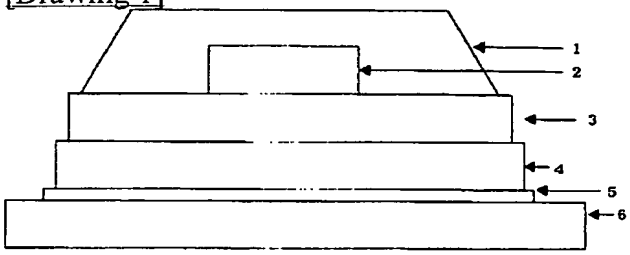
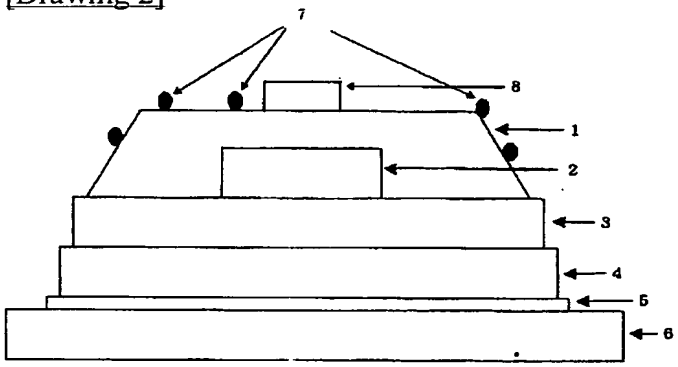
DRAWINGS

[Drawing 1]



[Drawing 2]



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(54)【発明の名称】　半導体用洗浄剤

(57)【要約】
【課題】　強誘電体材料を用いた素子の製造工程で、エッチング時などに発生する残渣物を除去するための半導体用洗浄剤を提供すること。
【解決手段】　強誘電体材料を用いた素子の製造工程で発生する残渣物を除去する際に使用する、ポリカルボン酸を含有する水溶液からなる半導体用洗浄剤。

【特許請求の範囲】
【請求項１】強誘電体材料を用いた素子の製造工程で発生する残渣物を除去する際に使用する、ポリカルボン酸を含有する水溶液からなる半導体用洗浄剤。
【請求項２】ポリカルボン酸が、シュウ酸である請求項１記載の半導体用洗浄剤。
【請求項３】更に、フッ素化合物を含有する請求項１記載の半導体用洗浄剤。
【請求項４】強誘電体材料が、タンタル酸ストロンチウムビスマスである請求項１記載の半導体用洗浄剤。
【発明の詳細な説明】
【０００１】
【発明の属する技術分野】本発明は強誘電体を使用した不揮発性メモリ製造工程で、エッチング時等に発生する残渣物の除去に使用する半導体用洗浄剤に関する。
【０００２】
【従来の技術】コンピューター等に多用されているメモリは、従来は電源を切ると記憶されていたデータが消去されるため、常時通電するかバックアップ用の電源が必要とされていた。しかし近年、強誘電体材料を使用した不揮発性メモリが開発された。この不揮発性メモリはファイルメモリ、パーソナルＩＣカード、移動体通信機器、携帯情報端末機器、ＡＶパソコンなどへの使用が考えられている。不揮発性メモリの要である強誘電体材料としては、ジルコン酸チタン酸鉛（ＰＺＴと略称される）、タンタル酸ストロンチウムビスマス（ＳＢＴと略称される）などが使用される。また、強誘電体を使用した不揮発性メモリの電極材料としては、❶電気抵抗が十分小さい、❷強誘電体材料との格子定数のミスマッチが小さい、❸耐熱性が高い、❹反応性が低い、❺拡散バリア性が高い、❻二酸化珪素などの下地および強誘電体との密着性が良いなどの特性が要求され、白金（Ｐｔ）、酸化ルテニウム（ＲｕＯｘ）、酸化イリジウム（IrO_2）などが使用される。
【０００３】このため、不揮発性メモリ製造工程でエッチング時などに発生する残渣物は、これらの金属を含むものとなり、残渣物の除去が非常に難しいものとなっており、これらの残渣物を除去する技術が必要とされている。これらの残渣物を除去するためには、通常ヒドロキシルアミンを含有するアミン系剥離液などで除去する方法が一般的に実施されている。しかしながら、ヒドロキシルアミンを含有するアミン系剥離液は、安全性、環境の面で多くの問題点を有しており、さらに高温な条件下で使用しなければならない等の問題点も有している。
【０００４】
【発明が解決しようとする課題】本発明の課題は不揮発性メモリ製造工程でエッチング時などに発生する残渣物を除去する方法に使用する、安全で、かつ環境面でも優れた半導体用洗浄剤を提供することである。
【０００５】
【課題を解決するための手段】本発明者らは、前述の目的を解決するために鋭意検討を重ねた結果、ポリカルボン酸を含有する水溶液が、半導体用洗浄剤としてその目的に適合しうることを見出した。本発明はかかる知見に基づいて完成したものである。すなわち、本発明は、強誘電体材料を用いた素子の製造工程で発生する残渣物を除去する際に使用する、ポリカルボン酸を含有する水溶液からなる半導体用洗浄剤を提供するものである。
【０００６】
【発明の実施の形態】本発明の半導体用洗浄剤において用いられるポリカルボン酸は、単独で用いても、２種以上を組み合わせても良い。このようなポリカルボン酸として、シュウ酸、マロン酸、コハク酸、グルタル酸、アジピン酸、ピメリン酸、スペリン酸、アゼライン酸、セバシン酸、ウンデカンニ酸、ドデカンニ酸等の飽和ジカルボン酸類、マレイン酸、フマル酸、イタコン酸、シトラコン酸、メサコン酸、グルタコン酸等の不飽和ジカルボン酸が挙げられる。上記ポリカルボン酸の中で、特に好ましくは、シュウ酸である。本発明に使用されるポリカルボン酸の含有量は、特に制限はなく、状況に応じて適宜選択されるが、通常は０．１～１５重量％であり、好ましくは１～５重量％である。この量が０．１重量％未満では残渣物の除去速度が遅く、１５重量％を超えると、ポリカルボン酸が析出する等の問題が発生するため好ましくない。
【０００７】この洗浄剤による残渣物の除去方法としては、例えば洗浄剤中に、残渣物が生成した強誘電体材料を用いた基板を、浸漬する方法、洗浄剤中に上記基板を浸漬するとともに、超音波振動や撹拌羽根などにより、洗浄剤を撹拌する方法などを挙げることができる。また、洗浄剤の温度は残存している残渣物の状態から判断して適宜、選定すれば良く、通常、室温から沸点までの任意の温度で良いが、常温から９０℃が好ましく、特に２０～７０℃が好ましい。さらに除去処理時間は特に制限はなく、除去方法や洗浄剤の温度などに応じて適宜選択すれば良い。
【０００８】この洗浄液を使用して残渣物を除去した後に、使用するリンス液としては水で充分でありアルコールのような有機溶剤を使用する必要は無い。また、この洗浄剤に、残渣物の組成、性質に応じて適宜、界面活性剤、キレート剤、フッ素化合物等を添加しても良い。
【０００９】さらに、本発明の洗浄剤の残渣物の除去能を向上させる目的で、所望により、フッ素化合物を含有させることができる。このフッ素化合物としては、フッ酸、フッ化アンモニウム、フッ化水素酸、フッ化水素アンモニウム、ホウフッ化アンモニウムなどが挙げられる。
【００１０】このフッ素化合物は単独で用いても良く、２種以上を組み合わせて用いても良い。また、その含有量は特に制限は無く、状況に応じて適宜選択すれば良い

が、通常は0．００１～１０重量%で、好ましくは0．０１～１重量%である。０．００１重量%未満では、残渣物の除去能の向上が十分に発揮されないおそれがあり、また１０重量%を超えると、電極、Ｓｉ基板等の腐食を引き起こすおそれがある。

【００１１】

【実施例】次に、本発明を実施例により詳細に説明するが、本発明はこれらの例によってなんら限定されるものではない。なお、図１は強誘電体材料を使用したメモリの製造工程の一部を示している。図２は実施例および比較例で用いた、金属配線を形成した後の、残渣物が存在する素子の模式的断面図である。図１に示したメモリの製造工程の一部は、Ｓｉ基板６上に絶縁層５を設け、その上に下部電極４を形成する。さらに、その上に強誘電体材料３を形成し、ついで上部電極２を形成した後、絶縁層１で被ったものである。その後、ドライエッチング、O_2アッシングなどにより種々の金属配線８を形成してゆくが、その折に、図２に示したように、金属、有機物などを含む残渣物７が生成し、基板上に付着する。

【００１２】実施例１

図２に示される素子を、シュウ酸３．４重量%を含有する水溶液中に４０℃、５分浸漬し、その後超純水によりリンスを行い，乾燥後ＳＥＭ観察を行ったが残渣物は完全に除去されていることが確認された。

【００１３】実施例２

図２に示される素子を、シュウ酸３．４重量%を含有する水溶液である洗浄液中に５０℃、１分浸漬し，その後超純水でリンスを行い乾燥後ＳＥＭ観察を行ったが残渣物は完全に除去されていることが確認された。

【００１４】実施例３

図２に示される素子を、シュウ酸５．５重量%を含有する水溶液である洗浄液中に４０℃、５分浸漬を行った。その後超純水でリンスを行い乾燥後ＳＥＭ観察を行ったが残渣物は完全に除去されていることが確認された。

【００１５】実施例４

図２に示される素子を、シュウ酸３．４重量%とフッ化アンモニウム０．２重量%を含有する水溶液である洗浄液中に４０℃、１分浸漬し，その後超純水でリンスを行い乾燥後ＳＥＭ観察を行ったが残渣物は完全に除去されていることが確認された。

【００１６】比較例１

図２に示される素子を、クエン酸３．４重量%を含有する洗浄液中に５０℃、１０分浸漬を行った。その後、超純水でリンスを行い乾燥後、ＳＥＭ観察を行ったが、残渣物の減少はほとんど観察されなかった。

【００１７】比較例２

図２に示される素子を、酒石酸３．４重量%を含有する洗浄液中に５０℃、１０分浸漬を行った。その後、超純水でリンスを行い乾燥後、ＳＥＭ観察を行ったが、残渣物の減少はほとんど観察されなかった。

【００１８】

【発明の効果】本発明の半導体用洗浄剤は、強誘電体材料を用いた素子の製造工程で発生する残渣物を、配線材料等を腐食する事なしに、容易に除去することができる。

【図面の簡単な説明】

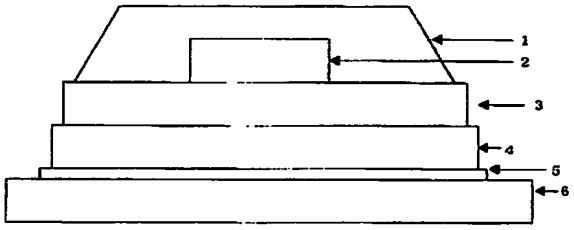
【図１】強誘電体材料を使用したメモリの製造工程の一部を示す、素子の模式的断面図である。

【図２】金属配線を形成した後の、残渣物が存在する状態の素子の模式的断面である。

【符号の説明】

１絶縁層、２上部電極、３強誘電体材料、４下部電極、５絶縁層、６Ｓｉ基板、７残渣物、８金属配線

【図１】



【図２】